

I. STRUCTURE ELUCIDATION OF EPANORIN AND A
SYNTHETIC APPROACH TO PINASTRINIC ACID

II. EMULSION OXIMATION OF SOME CARBONYL
COPOLYMERS OF BUTADIENE

BY

SAUL MARK COHEN

B.S., University of Massachusetts, 1948

M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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URBANA, ILLINOIS

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I. STRUCTURE ELUCIDATION OF EPANORIN AND A SYNTHETIC APPROACH TO PINASTRINIC ACID

INTRODUCTION

Epanorin is a lichen pigment first reported by Zopf (1) in 1900. Until the recent discovery by Nolan and co-workers (2) that the relatively rare compound contained nitrogen, very little was known about its structure. The analysis brought to three the total number of lichen pigments reported to contain nitrogen (2).

Pinastrinic acid is a lichen pigment of the same family whose structure is known (3). It is identical with vulpinic acid, except that an anisyl group is substituted for one of the phenyl rings. In attempting to synthesize this compound by a new route, it was hoped to investigate the scope of a new reaction (4) whereby pulvinic acid lactone is the product of the treatment of 2,5-diphenyl-3,6-dihydroxy-1,4-benzoquinone with lead tetraacetate. The necessary intermediate, therefore, was to be 2-*p*-anisyl-5-phenyl-3,6-dihydroxy-1,4-benzoquinone. The initial steps of the problem were accomplished successfully, and the final steps are to be found in the doctorate dissertation of Mr. William W. West at the University of Illinois.

DISCUSSION

Many of the properties of epanorin were observed to be similar to those of vulpinic acid, a known derivative of pulvinic acid lactone. Further deductions led to the treatment of pulvinic acid lactone with the methyl ester of L-leucine. The product, the methyl ester of L-N-pulvinylleucine, was obtained in a yield of 36 per cent and was proven to be epanorin by a mixed melting point plus a comparison of infrared spectra with the natural product. The pigment possesses a very low optical rotation, the $[\alpha]^{25}_D$ in chloroform being measured to be $-0.82 \pm 0.01^\circ$ ($c = 1.22$).

In the preparation of pinastrinic acid, treatment of benzoquinone with *p*-anisidinediazonium chloride gave 2-*p*-anisyl-1,4-benzoquinone in a yield of 30 per cent. Treatment of the product with benzene, aluminum chloride, and stannic chloride gave 2-*p*-anisyl-5-phenylhydroquinone, which was oxidized with nitrous acid to give 2-*p*-anisyl-5-phenyl-1,4-benzoquinone in 24 per cent yield. Bromination with excess bromine indicated the sensitivity of the ortho positions on the anisyl ring, giving 2-(3,3'-dibromoanisyl)-3,6-dibromo-5-phenyl-1,4-benzoquinone in 69 per cent yield. Hydrolysis of the brominated product yielded 2-(3,3'-dibromoanisyl)-5-phenyl-3,6-dihydroxy-1,4-benzoquinone in quantitative yield.

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II. EMULSION OXIMATION OF SOME CARBONYL COPOLYMERS OF BUTADIENE

INTRODUCTION

For use in further study, it was desired to obtain copolymers of various α -alkylacrolein oximes and butadiene. Copolymers of acrolein oxime are reported by Tuerck and Lichtenstein (1).

DISCUSSION

Copolymerization of acrolein oxime and acrolein oxime

acetate with butadiene produced no elastomers. Both of the compounds acted as inhibitors in free radical polymerization reactions.

An alternative route for obtaining the oxime copolymers was considered possible by copolymerizing the precursor carbonyl monomers with butadiene and oximating the carbonyl groups of the resulting copolymer in the original emulsion. Copolymerization of acrolein and methacrolein with butadiene produced copolymers relatively insoluble in benzene but soluble in chloroform. All the inherent viscosities were very low, of the order of 0.1. If the addition of the methacrolein to the system was delayed, some increase in the inherent viscosity was obtained. The chloroform solubility and low inherent viscosities are attributed to the trimerization of the aldehyde groups.

To break up the postulated trimeric form of the monomers, the acetals were prepared. Both acrolein diethylacetal and methacrolein diethylacetal gave copolymers with butadiene which had good solubility and viscosity characteristics but which contained only a small amount of the acetals. With those copolymers, the presence of easily-cleaved peroxide linkages in the chains was overcome by the rigorous elimination of all traces of oxygen from the copolymerization system.

A method was devised for the emulsion oximation of carbonyl copolymers of butadiene. By this method, oximation of polybutadiene in emulsion produced a polymer containing some nitrogen. The presence of the nitrogen is attributed to a reaction between hydroxylamine and peroxide-induced functional groups in the polymer. The carbonyl groups of benzalacetophenone-butadiene copolymer did not undergo reaction with hydroxylamine in emulsion; those of cinnamaldehyde-butadiene copolymer indicated slight oximation; and those of methyl isopropenyl ketone-butadiene copolymer underwent partial oximation. With this last copolymer, excluding the nitrogen contained in the polybutadiene portion of the molecules, the methyl isopropenyl ketoxime was cal-

culated to constitute 3.7 per cent of the copolymer by weight.

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VITA

The author was born October 6, 1924, in Springfield, Massachusetts. He received his elementary and secondary education in the public schools of that city, and in September 1942, he entered the University of Massachusetts. On April 5, 1943, he enlisted in the United States Army Air Force, and he served with this branch of the armed forces till his discharge on September 24, 1945. He then re-entered the University of Massachusetts and received a B. S. degree in June 1948. In September 1948, he entered the Graduate School of the University of Illinois, and he received a M. S. degree from that institution in August 1949. From October 1950 until his final graduation from the University of Illinois, he held a special research assistantship under the Government Synthetic Rubber Program, sponsored by the Reconstruction Finance Corporation.

